

UV-CURABLE POLYOLS

FIELD OF THE INVENTION

The present invention relates in general to polyols, and more specifically, to ultraviolet (UV)-curable polyols made by co-polymerizing an unsaturated carboxylic acid or anhydride, an alkylene oxide and a hydroxy functional compound in the presence of a double metal cyanide (DMC) complex catalyst. The present invention also relates to prepolymers made from the inventive polyols and to thin film articles made from those prepolymers.

BACKGROUND OF THE INVENTION

Natural rubber latex (NRL) is the material of choice in many applications requiring soft, thin-walled elastic articles, such as medical examination and scientific gloves. NRL articles typically are made by dipping a mandrel, pre-coated with a coagulant, into an aqueous rubber emulsion. To produce NRL gloves which are adequately strong, but which do not have pinholes, the dipped NRL gloves must be about 0.18 to about 0.20 mm thick. Although gloves made from NRL possess an excellent combination of flexibility, high elongation at break, tensile strength and a low degree of creep, in recent years the use of NRL has been under attack because of increased instances of allergic reactions caused by proteins and vulcanization accelerator residues present in NRL.

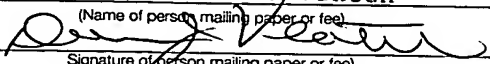
The manufacture of medical exam and scientific gloves from polyurethane is known to those skilled in the art. For example, U.S. Pat. No. 4,463,156, issued to McGary, Jr., et al., discloses a soft, low modulus, non-crystalline segmented polyurethane with a 100% modulus less than about 250 psi, initial tensile set less than about 30% and tensile strength of about 3500 to 6500 psi. McGary, Jr. et al. teach balancing the percent hard segment and the degree of cross-linking within the ranges of 14 to

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25% hard segment and 5,000 to 30,000 molecular weight per cross-link in a segmented polyurethane. The polyurethane of the '156 patent is said to produce a flexible glove for use by surgeons and others which is easily donned and comfortable on the hand.

5 A waterborne dispersion of a polyurethane polymer said to be useful as a film having improved mechanical properties is disclosed by Snow, et al. in U.S. Pat. No. 6,017,997. The film is said to have properties comparable to rubber including, a percentage elongation greater than 700%, a tensile strength greater than 3,500 psi, a 100% modulus below
10 450 psi, a 300% modulus below 700 psi, and a 500% modulus below 1,500 psi. This film can be prepared in the absence of a solvent, thus making it attractive for a variety of protection products for medical and industrial applications such as gloves, condoms, catheters, and the like. However, the films of Snow et al. are crosslinked by the urethane reaction;
15 therefore, the residual NCO may cause allergic reactions on human skin.

Polyurethane is typically made by reacting a polyol with an isocyanate. The majority of polyoxyalkylene polyether polyols are polymerized through base catalysis. For example, polyoxypropylene diols are prepared by the base-catalyzed oxypropylation of a difunctional
20 initiator such as propylene glycol. During base-catalyzed oxypropylation, a competing rearrangement of propylene oxide to allyl alcohol continually introduces an unsaturated, monofunctional, oxyalkylatable species into the reactor. The oxyalkylation of this monofunctional species yields allyl-terminated polyoxypropylene monols. The rearrangement is discussed in
25 BLOCK AND GRAFT POLYMERIZATION, Vol. 2, Ceresa, Ed., John Wiley & Sons, pp. 17-21. Unsaturation is measured in accordance with ASTM D-2849-69 "Testing Urethane Foam Polyol Raw Materials," and expressed as milliequivalents of unsaturation per gram of polyol (meq/g). Due to this continual creation of allyl alcohol and its subsequent oxypropylation, the
30 average functionality of the polyol mixture decreases and the molecular weight distribution broadens. Base-catalyzed polyoxyalkylene polyols

contain considerable quantities of lower molecular weight, monofunctional species. In polyoxypropylene diols of 4,000 Dalton (Da) molecular weight, the content of monofunctional species may be between 30 and 40 mole percent. In such cases, the average functionality is lowered to about 1.6
5 to 1.7 from the nominal, or theoretical functionality of 2.0. In addition, base-catalyzed polyols have a high polydispersity (M_w/M_n) due to the presence of the substantial, low molecular weight fractions.

Lowering unsaturation and the attendant high monol fraction in polyoxypropylene polyols has been touted as a means of providing
10 polyurethane compositions with improved properties. Often, formulations must be chosen to balance conflicting properties. For example, increases in tensile strength are often accompanied by a decrease in elongation.

Therefore, a need exists in the art for a polyol that will provide prepolymers that can be used to make thin films having the desired
15 properties of natural rubber latex (NRL) including low modulus, high elongation, high tensile strength and solvent resistance, without the drawbacks associated with NRL such as allergic reactions.

SUMMARY OF THE INVENTION

20 Accordingly, the present invention alleviates the need in the art by providing an ultraviolet (UV)-curable polyol made by co-polymerizing an alkylene oxide, an unsaturated carboxylic acid or anhydride and a hydroxy functional compound in the presence of a double metal cyanide (DMC) complex catalyst. The inventive ultraviolet (UV)-curable polyols can be
25 combined with an isocyanate and at least one of a photo-initiator and a cross-linking agent to produce prepolymers for making thin films having the desired properties of natural rubber latex (NRL) including low modulus, high elongation, high tensile strength and solvent resistance, without the drawbacks associated with NRL such as allergic reactions. An ultraviolet
30 (UV) cure substantially improves isopropanol (IPA) resistance of those

gloves or films including the inventive ultraviolet (UV)-curable polyols without adversely affecting the tensile properties.

These and other advantages and benefits of the present invention will be apparent from the Detailed Description of the Invention herein
5 below.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described for purposes of illustration and not limitation. Except in the operating examples, or where
10 otherwise indicated, all numbers expressing quantities, percentages, OH numbers, functionalities and so forth in the specification are to be understood as being modified in all instances by the term "about."

The term "NCO content" herein refers to the isocyanate group content of the prepolymer, before chain extension. The term "molecular
15 weight" means number average molecular weight unless indicated otherwise. The number average molecular weights for the polyether glycols are each determined from the hydroxyl number of the polyether glycol as measured by the imidazole-pyridine catalyst method described by S. L. Wellon et al., "Determination of Hydroxyl Content of Polyurethane
20 Polyols and Other Alcohols", ANALYTICAL CHEMISTRY, Vol. 52, No. 8, pp. 1374-1376 (July 1980). The molecular weights and equivalent weights given herein in Da (Daltons) are number average molecular weights and number average equivalent weights, respectively, unless specified otherwise.

25 The present invention provides an ultraviolet (UV)-curable polyol comprising the reaction product of 30 to 70 wt. % of a hydroxy functional compound having a functionality of 2 to 3, 1 to 10 wt. % of an unsaturated carboxylic acid or anhydride; and 20 to 69 wt. % of an alkylene oxide, wherein the reaction occurs in the presence of a double metal cyanide
30 (DMC) catalyst.

The co-polymers of alkylene oxide and unsaturated carboxylic acids or anhydrides of the present invention are photo-curable. The inventors have found, surprisingly, that unsaturated carboxylic acids and anhydrides such as cis-1,2,3,6-tetrahydrophthalic anhydride can co-polymerize well
5 with alkylene oxides such as propylene oxide (PO) in the presence of a double metal cyanide (DMC) catalyst. This conversion is complete even at low concentrations of monomer.

The hydroxy functional compound may be polypropylene oxide, polyethylene oxide, polybutylene oxide, copolymers of propylene oxide
10 and ethylene oxide, copolymers of propylene oxide and butylene oxide, copolymers of butylene oxide and ethylene oxide, and mixtures thereof. Preferred as the hydroxy functional compound is polyoxypropylene. The hydroxy functional compound is preferably used in amounts of 30 to 70 wt. %, more preferably 30 to 60 wt. % and most preferably 40 to
15 60 wt. %. The functionality of the hydroxy functional compound is from 2 to 3.

The unsaturated carboxylic acid or anhydride may be any compounds bearing at least one C=C group and at least one carboxylic acid or anhydride group. Examples include cis-1,2,3,6-tetrahydrophthalic
20 acid and anhydride and maleic acid and anhydride. Preferred as the unsaturated carboxylic acid or anhydride is cis-1,2,3,6-tetrahydrophthalic anhydride. The unsaturated carboxylic acid or anhydride may be used in amounts of 1 to 10 wt. %, more preferably 1 to 5 wt. % and most preferably 2 to 5 wt. %.

25 The alkylene oxide may be propylene oxide, ethylene oxide, butylene oxide, the like, and mixtures thereof. Preferably, the alkylene oxide is propylene oxide. The alkylene oxide may be used in amounts of 20 to 60 wt. %, more preferably 20 to 50 wt. % and most preferably 25 to 50 wt. %.

30 Recent advances in DMC catalysts and polyoxyalkylation processes have enabled the practical preparation of ultra-low unsaturation

polyoxypropylene polyols. High molecular weight polyols, for example those in the 4,000 Da to 8,000 Da molecular weight range, typically exhibit unsaturation in the range of 0.004 to 0.007 meq/g if catalyzed by these DMC catalysts. At those levels of unsaturation, the amount of

5 monofunctional species is only 2 mole percent or less. Moreover, gel permeation chromatography (GPC) analysis shows those polyols to be virtually monodisperse, often exhibiting polydispersities less than 1.10. A number of such polyols have been commercialized, by the assignee of the present disclosure, as ACCLAIM polyols. These ultra-low unsaturation

10 polyols have been found to be quantitatively different than both conventional polyols and low unsaturation polyols.

Therefore, the catalyst used to produce the ultraviolet (UV)-curable polyol of the present invention is preferably a double metal cyanide (DMC) catalyst, such as those disclosed in U.S. Pat. Nos. 5,470,813 and

15 5,482,908, the entire contents of which are incorporated herein by reference. Through the use of the catalysts disclosed in those references, unsaturation levels in the range of 0.004 to 0.008 may be achieved.

Following preparation, the inventive ultraviolet (UV)-curable polyol may be reacted with an excess of the desired diisocyanate, preferably

20 under a nitrogen atmosphere at slightly elevated temperature, i.e., from 50°C to 100°C more preferably from 60°C to 90°C. The reaction of the isocyanate with the ultraviolet (UV)-curable polyol of the present invention may be catalyzed, but it is generally preferred that the reaction take place without catalysis. The reaction proceeds until the point where the

25 isocyanate content becomes constant. The isocyanate-terminated prepolymers of the present invention preferably have an NCO group content of from 0.1 to 10 wt. %, more preferably from 0.5 to 5 wt. % and most preferably from 1 to 2 wt. %.

Both aliphatic and aromatic di- and polyisocyanates may be used to

30 prepare the prepolymers of the present invention. Diisocyanates are preferred, however it is within the scope of the invention to include a minor

- amount, i.e., not more than approximately 20 mole percent, of a tri- or higher-functionality isocyanate. Preferred isocyanates include, but are not limited to, linear aliphatic isocyanates such as 1,2-ethylene diisocyanate, 1,3-propylene diisocyanate, 1,4-butylene diisocyanate, 1,6-hexylene diisocyanate, 1,8-octylene diisocyanate, 1,5-diisocyanato-2,2,4-trimethylpentane, 3-oxo-1,5-pentane diisocyanate, and the like; cycloaliphatic diisocyanates such as isophorone diisocyanate, the cyclohexane diisocyanates, preferably 1,4-cyclohexane diisocyanate, fully hydrogenated aromatic diisocyanates such as hydrogenated tetramethylxylylene diisocyanate, hydrogenated toluene diisocyanates, and hydrogenated methylene diphenylene diisocyanates; and aromatic diisocyanates such as the toluene diisocyanates, particularly the 2,4-isomer, the methylene diphenylene diisocyanates, particularly 2,4' and 4,4'-methylene diphenylene diisocyanate (2,4'- and 4,4'-MDI, respectively), tetramethylxylylene diisocyanate, and the like. Less preferred aromatic diisocyanates include the polymethylene polyphenylene polyisocyanates having functionalities greater than two. Also preferred are modified diisocyanates prepared by reacting one or more diisocyanates with themselves, or with a low molecular weight isocyanate reactive compound to form urea-modified, urethane-modified, carbodiimide-modified, allophanate-modified, uretonimine-modified, biuret-modified, and other modified isocyanates, many of which are commercially available. More than one isocyanate may be used. Particularly preferred is 2',4-toluene diisocyanate (2',4-TDI).
- 25 The inventive prepolymers may also include at least one of a photo-initiator and a cross-linking agent. Preferred photo-initiators include, but are not limited to, benzophenones and acetophenones. Examples are alpha-hydroxyalkylphenylketones, benzoin alkyl ethers and benzil ketals, monoacylphosphine oxides, and bisacylphosphine oxides.
- 30 Preferred cross-linking agents include, but are not limited to, di- or multi-ethylenic monomers. Examples are divinylbenzene, propylene glycol

di acrylate or methacrylate, trimethylolpropane triacrylate, the like, and mixtures thereof.

The amount of photo-initiator(s) is not particularly critical, but may be from 0.3 to about 10 wt. %, and more preferably, from 1 to about 5 wt. % of the final product.

The inventive prepolymers can be used to produce thin films which may be fashioned into medical exam and scientific gloves by methods known to those skilled in the art. Thin films prepared from a water dispersion of the diol-based prepolymer of the present invention show a significant improvement in isopropanol (IPA) resistance. One of the advantages of ultraviolet (UV) cure, as shown in the instant disclosure, was that this IPA resistance improved without any significant degradation in the physical properties of the film (tensile, modulus).

The present invention is further illustrated, but is not to be limited, by the following examples.

EXAMPLES

Polyol A

A 4,000 MW copolymer of propylene oxide and cis-1,2,3,6-tetrahydrophthalic anhydride using a monomer mixture of 3.9 wt. % of tetrahydrophthalic anhydride in propylene oxide was prepared by charging a 1.5-liter reactor with a 450 MW polyoxypropylene diol (105 g) starter and DMC catalyst prepared essentially by the method of U.S. Pat. No. 5,482,908 (0.0504 g, 50 ppm based on the amount of finished polyol product). The mixture was stirred and heated to 130°C, and was stripped under vacuum for 30 minutes to remove traces of water from the diol starter. After stripping, a mixture of propylene oxide and cis-1,2,3,6-tetrahydrophthalic anhydride (3.9 wt. % of tetrahydrophthalic anhydride) (15 g) was fed to the reactor, initially under a vacuum of about 30 in. Hg, and the reactor pressure was monitored. Additional monomer mixture was not added until an accelerated pressure drop occurred in the reactor. The

pressure drop is indicative of catalyst activation. After catalyst activation was verified, the remaining mixture of propylene oxide and cis-1,2,3,6-tetrahydrophthalic anhydride (860 g) was added gradually over about four hours. After monomers addition was completed, the reactor mixture was
5 held at 130°C until a constant pressure was observed. Residual unreacted monomers were stripped under vacuum at 80°C for 30 minutes from the polyol product.

The hydroxyl number and viscosity of the product were measured by standard methods and were 30 mg KOH/g and 1003 cps, respectively.

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Polyol B

The procedure of Example 1 was followed to produce a 4,000 MW copolymer of propylene oxide and cis-1,2,3,6-tetrahydrophthalic anhydride using a monomer mixture of 1.9 wt. % of tetrahydrophthalic anhydride in
15 propylene oxide, by using a monomer mixture of 1.9 wt. % of tetrahydrophthalic anhydride in propylene oxide. The hydroxyl number and viscosity of the product were 28.4 mg KOH/g and 1163 cps, respectively.

The process for making a glove from the polyols described above
20 involved five discrete steps:

- (1) making a prepolymer;
- (2) neutralizing the prepolymer;
- (3) chain extension;
- (4) dispersing the prepolymer in water; and
- 25 (5) glove dipping.

The first two steps are detailed below:

Prepolymer & Neutralization

The prepolymer reaction and neutralization steps were conducted in
30 a standard, unbaffled round-bottom flask, containing a single "half-moon"

shaped TEFLON agitator. The reactor was heated via electric heating mantle and temperature control is generally within $\pm 1^{\circ}\text{C}$.

Prior to the experiment, the reactor was charged with the polyol (508.5 g of diol (Polyol A or B), 4.0 g of LHT-240 (a 700 molecular weight polyoxypropylene polyol available from Bayer Polymers LLC), 70 g of n-methyl pyrrolidinone (NMP), and 24 g of dimethylolpropionic acid (DMPA). This mixture was heated to 100°C to dissolve the DMPA and evacuated to 50 mm Hg to reduce the water level to about 100-150 PPM. A Karl Fisher water analysis was conducted at the end of the strip to confirm the final water concentration. Nitrogen sparging was used both to control the vacuum at about 50 mm Hg and help strip out the water. When the water level reached the desired level, the reactor was cooled to about 60°C . 2',4-toluene diisocyanate (2',4-TDI) (93.5 g), available from Bayer Polymers LLC as MONDUR TDS, and trimethylol propane triacrylate (10.0 g) were added to the polyol. Addition of the TDI resulted in about a $15\text{-}20^{\circ}\text{C}$ exotherm, after which the reactor temperature was set to the desired run temperature of 80°C . The reactor was maintained at 80°C and atmospheric pressure, until all of the polyol and DMPA reacted with isocyanate (target NCO). The following prepolymer formulation was the basis for the work described herein: 1.60 NCO/OH (with 2',4-TDI as the isocyanate), 1.25% COOH (with DMPA as the carboxylate) and 10% NMP (solvent).

After the reaction was completed (target NCO value reached), the reactor was cooled to about $30\text{-}40^{\circ}\text{C}$ and triethylamine (TEA) (17.25 g) was added to neutralize the prepolymer. Sufficient TEA was added to neutralize 95-100% of the carboxylate (DMPA). The prepolymer was mixed for 15-30 minutes to ensure completion of reaction with the TEA. The neutralized prepolymer was poured into a dispersion vessel containing water (see below).

Dispersion and film preparation

A dispersion vessel (an open, unheated, baffled, cylindrical steel tank) was precharged with sufficient deionized water to achieve the targeted percent solids (about 40%) and agitated (about 10 hp/1000 gal
5 with a COWLES disperser). The neutralized prepolymer was added to the water (over 2-3 minutes). The dispersion was agitated for about 60 minutes before pouring into a storage container. During this step, a small layer of foam (0.25 in. to 1 in.) formed on the surface.

Dispersions may be evaluated by making a film or dipping gloves.
10 As the process of making a film is fairly simple, it was used to evaluate the physical properties of the dispersions of the present invention. In this process, the dispersion was spread uniformly onto a flat surface (glass or MYLAR), allowed to dry overnight and heated at 120°C for about 45 minutes, after which time the film was analyzed for IPA resistance and
15 tensile properties. The standard evaluation was as follows:

The "Percent Isopropanol (IPA) Swell" is a test in which a one-inch diameter circle was stamped out from a section of film or glove, which is 0.005-0.007 in. thick. The sample was soaked in a beaker of 70% IPA/30% water at ambient temperature for a specified amount of time,
20 such as 10 minutes. The diameter of the circle was measured as a function of time. If, for example, the diameter increased from 1 in. to 1.25 in., the percent swell was reported as 25%. Ideally, the swell should be negligible, although a value less than 50% is considered by those in the art to be reasonable. It is important that any sample evaluated for Percent
25 IPA Swell be within the thickness range given above, because the Percent Swell is very sensitive to thickness. Thick samples tend to swell less, because the IPA does not have sufficient time to diffuse through the sample.

The "300% IPA Stretch Test" involved stretching a rectangular
30 section of film (generally 0.005-0.007 in. thick) to four times the original length (300%), while briefly rubbing the surface of the film with a small

towelette moistened with IPA/water. The film was maintained in the stretched position until it broke or until 2 minutes passed (whichever occurred first). If the film did not break within two minutes, the IPA resistance was considered good.

- 5 Tensile strength (psi) and elongation (%) data at break, and modulus at 100% (psi) were determined according to ASTM D412 using an INSTRON universal testing machine. Where appropriate, elongation was recorded using an elastomeric extensometer. In some cases, it was recorded using one-inch benchmarks and an elongation ruler or via jaw separation.
- 10

Table I

Polyol used in prepolymer	UV Cure (min.)	300% IPA Stretch (sec.)	10-Min. IPA % Swell	Tensile Strength (psi)	Percent Elongation	100% Modulus (psi)
A	None	20	100	>1000	1100	130
A	20	>120	50	>1000	1100	86
B	None	>120	50	1621	1050	143
B	3	>120	50	1898	924	176
B	5	>120	31	1624	881	139
B	6	>120	31	1275	801	145

15 Prepolymers were made with trimethylolpropane triacrylate and 2,2-dimethoxy-1,2-diphenylethan-one (CIBA 651) as photo-initiators. Swell test conducted in 70% IPA/30% water. Film thickness is about 0.0074 inch.

- Thin films prepared from a water dispersion of the prepolymers made with the inventive polyols showed a significant improvement in IPA resistance. The IPA resistance of the film was measured as the percent swell of the film, after being soaked in a 70/30 IPA/water solution at ambient temperature for 10 minutes. As can be appreciated by reference to Table I, the control, which was the film made without any UV cure, showed a 100% swell after IPA soak (Polyol A). After UV cure, the film swelled only 50% in the IPA soak. Again by reference to Table I, with Polyol B, the swell was also reduced after the UV cure. One of the advantages of the UV cure, as shown in Table I is the improvement of IPA
- 20
- 25

resistance without any significant degradation in the physical properties of the film (tensile, elongation and modulus).

5 The inventors have made a series of 28-OH triols and diols with two to four percent by weight of cis-1,2,3,6-tetrahydrophthalic anhydride randomly distributed on the polyol backbone. These polyols were UV-curable through the unsaturation of the anhydride. The inventors have also found that the cross-linking reaction was enhanced when a small amount of cross-linking agent such as trimethylolpropane triacrylate was used in addition to the photo-initiator.

10 The foregoing examples of the present invention are offered for the purpose of illustration and not limitation. It will be apparent to those skilled in the art that the embodiments described herein may be modified or revised in various ways without departing from the spirit and scope of the invention. The scope of the invention is to be measured by the appended
15 claims.